# Part II. Functional Polymers for Semiconductor Applications

## Outline of Part

Polymeric Insulator for Semiconductor Applications

- ☐ Introduction of Silicone Chemistry
- ☐ Theory of Sol-Gel Chemistry
- ☐ Organic-Inorganic Hybrid Polymer
- ☐ Semiconductor Insulating Materials
- ☐ Nanoporous Polysiloxane Materials
- ☐ Summary of Future Trends

# History of Silicone Chemstry

*1824년 규소의 발견 – 최초의 염화규소화합물 $SiCl_4$의 합성

*1864년 최초의 유기규소화합물의 합성

$$SiCl_4 + Zn(CH_2CH_3)_2 \longrightarrow Si(CH_2CH_3)_4$$

*1938년 최초의 페닐실리콘 개발 (Corning Glass)

*1940년 메틸클로로실란의 직접합성법 개발 (GE)

*1943년 Dow Corning사 설립

*1965년 Union Carbide사 실리콘 사업시작

*1950년 반도체 실리콘용 고순도 규소생산

*1970년 광섬유용 $SiCl_4$ 정제

*1980년 실리콘 농약 개발

*1990년 Silsesquioxane 개발

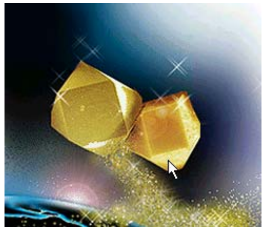
# Abundances of Elements

| Atomic No. | Symbol | (%) |
|---|---|---|
| 1 | H | 0.90000 |
| 6 | C | 0.08000 |
| 7 | N | 0.03000 |
| 8 | O | 49.50000 |
| 9 | F | 0.03000 |
| 11 | Na | 2.60000 |
| 12 | Mg | 1.90000 |
| 13 | Al | 7.50000 |
| 14 | Si | 25.70000 |
| 15 | P | 0.10000 |
| 16 | S | 0.06000 |
| 17 | Cl | 0.20000 |
| 19 | K | 2.40000 |
| 20 | Ca | 3.40000 |
| 22 | Ti | 0.60000 |
| 23 | V | 0.02000 |
| 24 | Cr | 0.02000 |
| 25 | Mn | 0.10000 |
| 26 | Fe | 4.70000 |
| 27 | Co | 0.00200 |
| 28 | Ni | 0.00800 |
| 29 | Cu | 0.00700 |
| 30 | Zn | 0.01000 |
| 31 | Ga | 0.00200 |
| 32 | Ge | 0.00070 |
| 35 | Br | 0.00002 |

| Atomic No. | Symbol | (%) |
|---|---|---|
| 37 | Rb | 0.030000 |
| 38 | Sr | 0.030000 |
| 39 | Y | 0.003000 |
| 40 | Zr | 0.020000 |
| 42 | Mo | 0.000800 |
| 46 | Pd | 0.000001 |
| 47 | Ag | 0.000010 |
| 48 | Cd | 0.000020 |
| 49 | In | 0.000010 |
| 50 | Sn | 0.000100 |
| 51 | Sb | 0.000300 |
| 53 | I | 0.000030 |
| 55 | Cs | 0.000700 |
| 56 | Ba | 0.030000 |
| 58 | Ce | 0.005000 |
| 59 | Pr | 0.000600 |
| 60 | Nd | 0.002000 |
| 63 | Eu | 0.000100 |
| 74 | W | 0.003000 |
| 78 | Pt | 0.000005 |
| 79 | Au | 0.000005 |
| 80 | Hg | 0.000300 |
| 81 | Tl | 0.000200 |
| 82 | Pb | 0.002000 |
| 83 | Bi | 0.000200 |
| 92 | U | 0.000400 |

# Silicon

규소원소 (silicon)는 지표면에 가장 많은 산소 다음으로 두번째 많은 원소(25.7%)이지만, 자연속에 유리되어 존재하지 않고, 주로 산소와 결합된 산화물이나 규산염 상태로 존재한다. 광물질의 형태로는 다양하며, 예를 들어 $SiO_2$는 순도와 결정상태에 따라서 모래 , 석영, 수정, 규석, 부싯돌 그리고 단백석, 더 나아가 귀금속 마노, 벽옥등의 다양한 형태로 존재한다

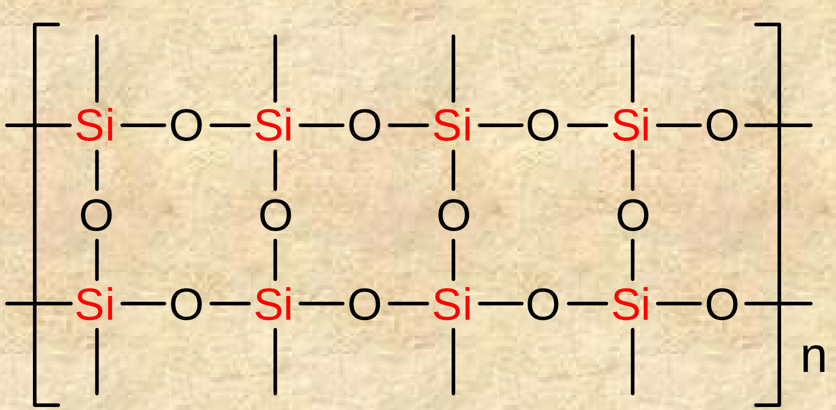


◆ 반짝인다고 다 금은 아니다. – 미국속담

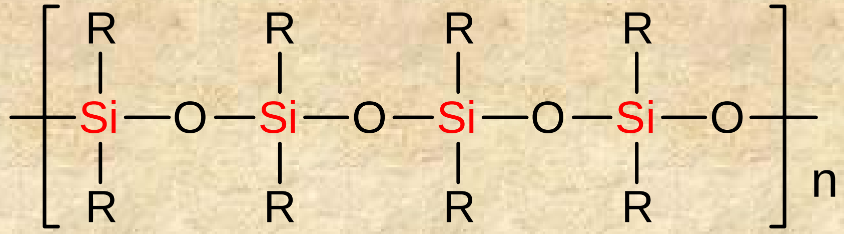
# Bond Energies

| Si Bonds | Energy (Kcal/mole) | C Bonds | Energy (Kcal/mole) |
|---|---|---|---|
| Si-Si | 53 | C-Si | 76 |
| Si-C | 76 | C-C | 82 |
| Si-H | 76 | C-H | 98 |
| Si-O | 108 | C-O | 85 |
| Si-N | 77 | C-N | 73 |
| Si-F | 135 | C-F | 116 |
| Si-Cl | 91 | C-Cl | 81 |
| Si-Br | 74 | C-Br | 68 |
| Si-I | 56 | C-I | 51 |

# Silicon Based Polymer



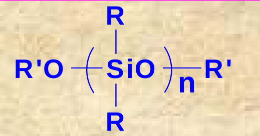
Silica



$$\left[\mathrm{SiR_2{-}O{-}SiR_2{-}O{-}SiR_2{-}O{-}SiR_2{-}O}\right]_n$$

Silicone Oil

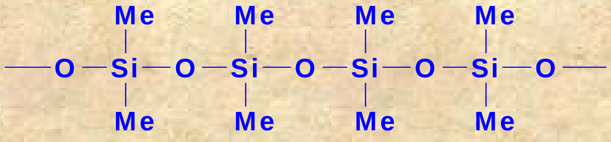
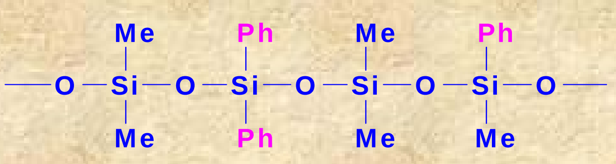
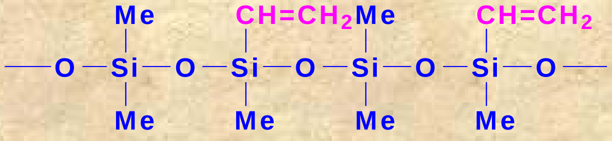
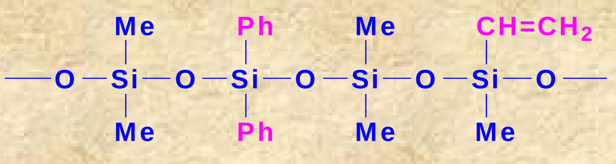
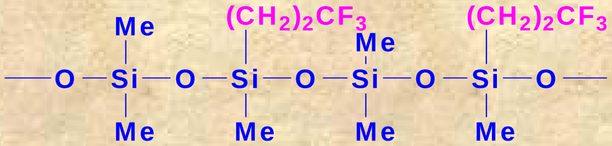
# Polsiloxane



$R'O\left(\underset{R}{\overset{R}{|}}\!\!\!\!\!\!\underset{|}{\overset{|}{Si}}O\right)_n R'$

$R = -Me, -Ph, -CH{=}CH_2, -CH_2CH_2CF_3$

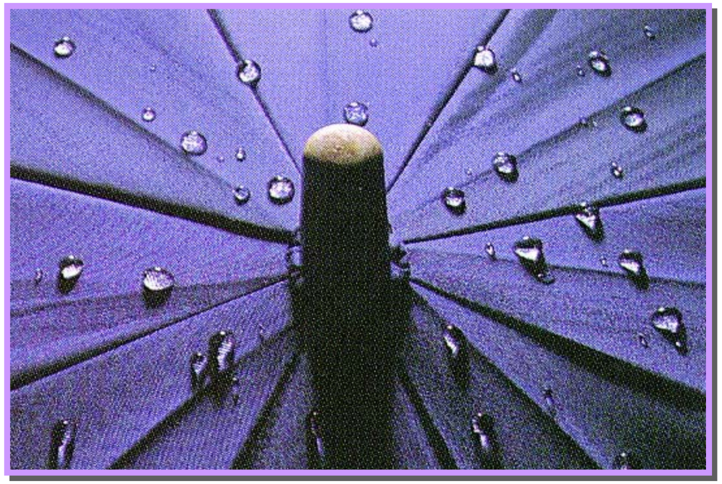
$R' = H, SiMe_3$

| Silicone Gums | Molecular Structures | ASTM Crassification |
|---|---|---|
| **Dimethyl Polysiloxane** |  $-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-$ | Si |
| **Methyl Phenyl Polysiloxane** |  $-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{Ph}{Si}}-O-$ | P Si |
| **Methyl Vinyl Polysiloxane** |  $-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{CH=CH_2}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{CH=CH_2}{Si}}-O-$ | V Si |
| **Methyl Phenyl Vinyl Polysiloxane** |  $-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Ph}{\overset{Ph}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{CH=CH_2}{Si}}-O-$ | PV Si |
| **Methyl Trifluoropropyl Polysiloxane** |  $-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{(CH_2)_2CF_3}{Si}}-O-\underset{Me}{\overset{Me}{Si}}-O-\underset{Me}{\overset{(CH_2)_2CF_3}{Si}}-O-$ | F Si |

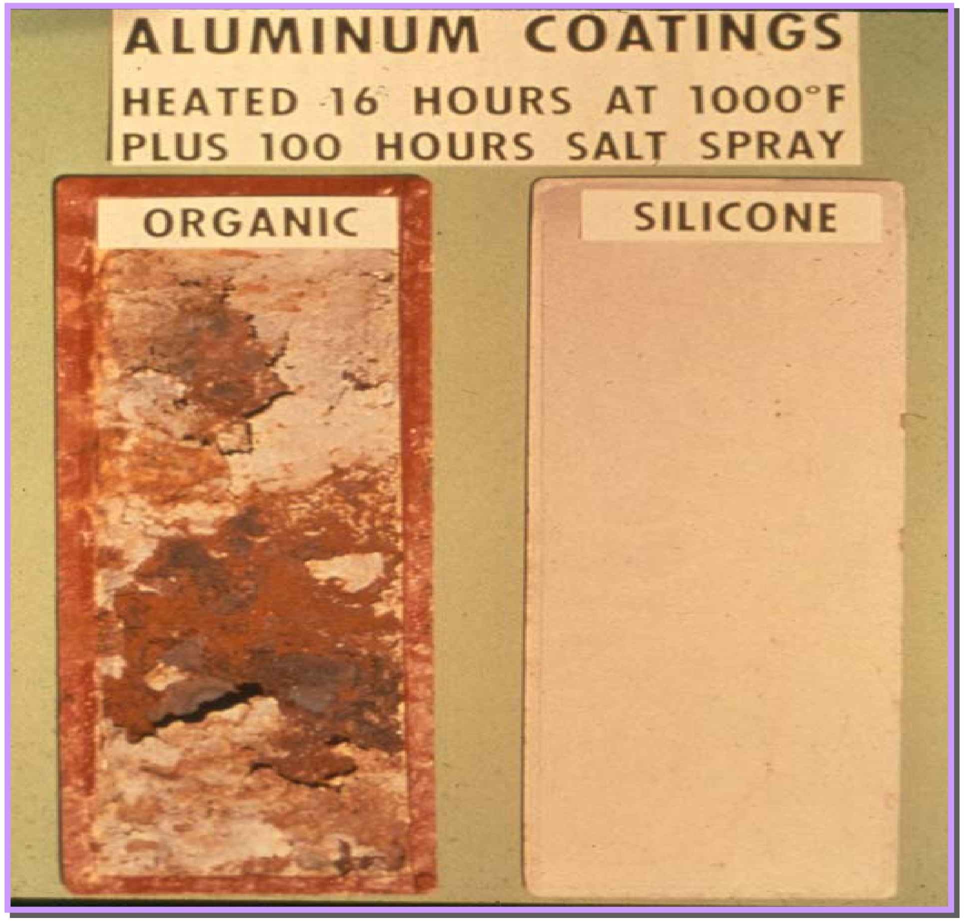
# Characteristics of Si based Compounds

- * 내열성 (+315 $^{o}$C)
- * 내한성 (절연온도특성 -125 $^{o}$C)
- * 내 약품성 (무독성)
- * 전기적인 절연성 (내 아크성)
- * 내후성 (내 자외선, 내 오존성, 내 방사능성)
- * 발수성
- * 난연성
- * 압축특성
- * 화학적 불활성

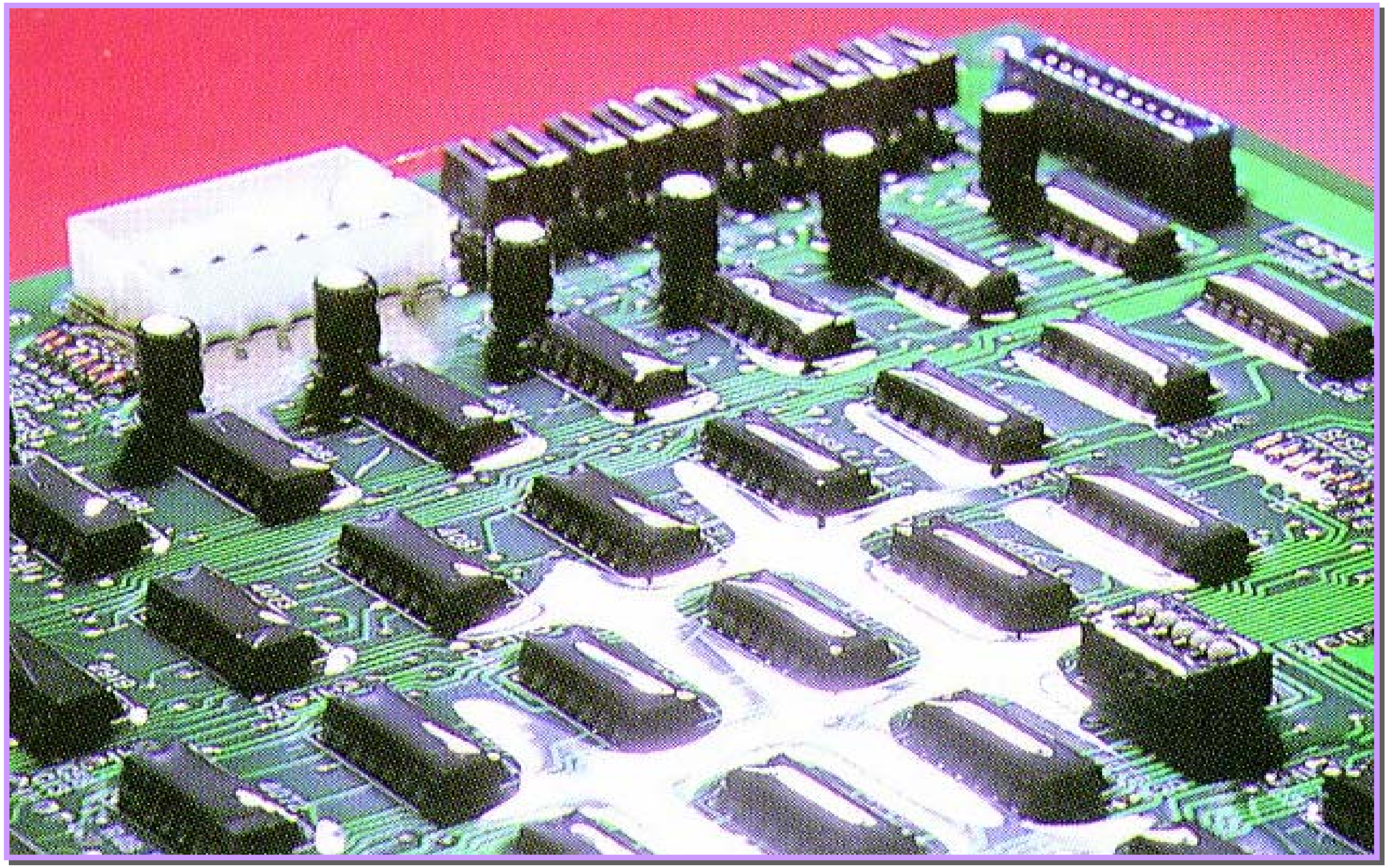
# Water Repellent & Softner



# Silicone Resin vs Organic Resin

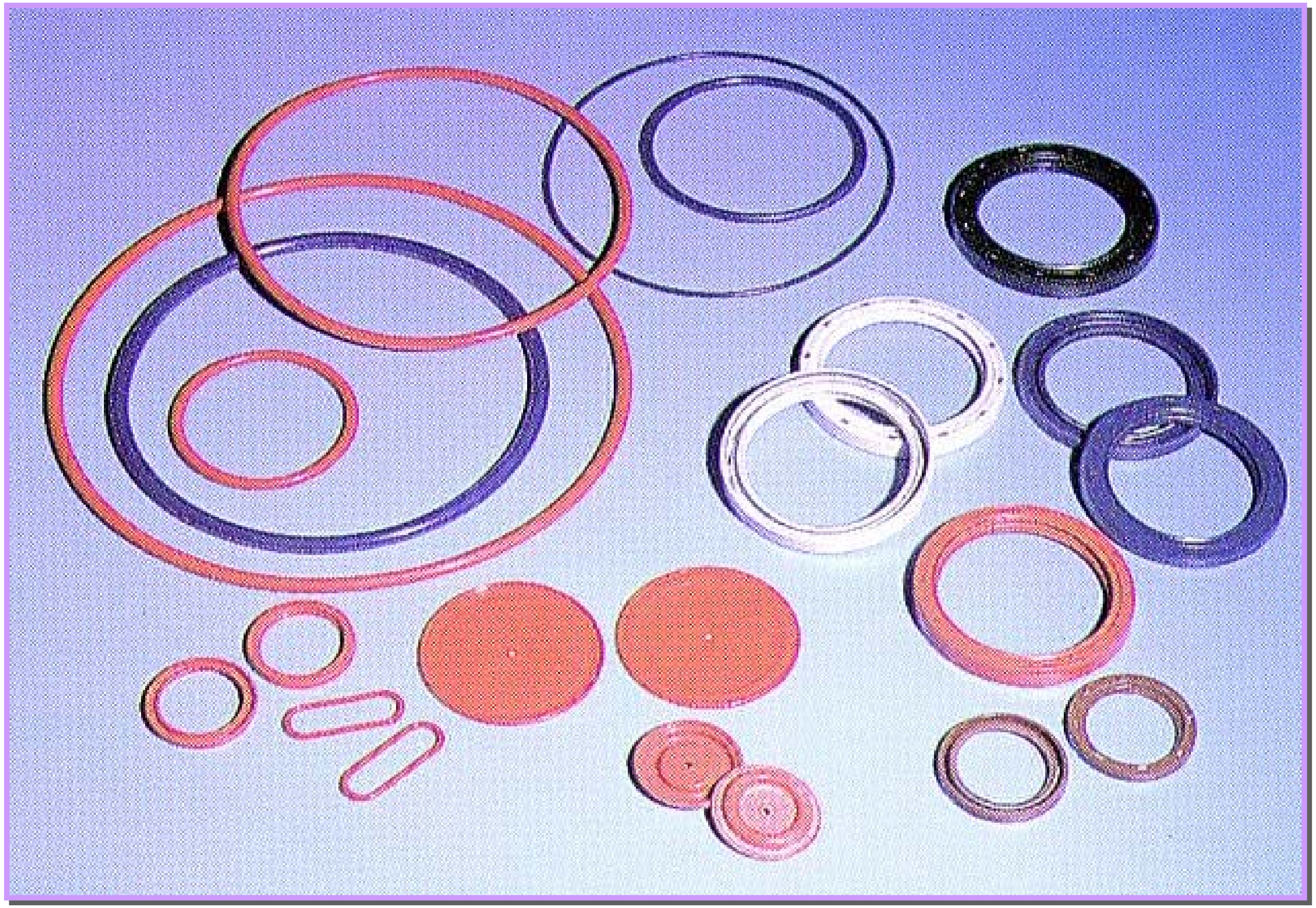


# Moisture Resistant Surface Treatment

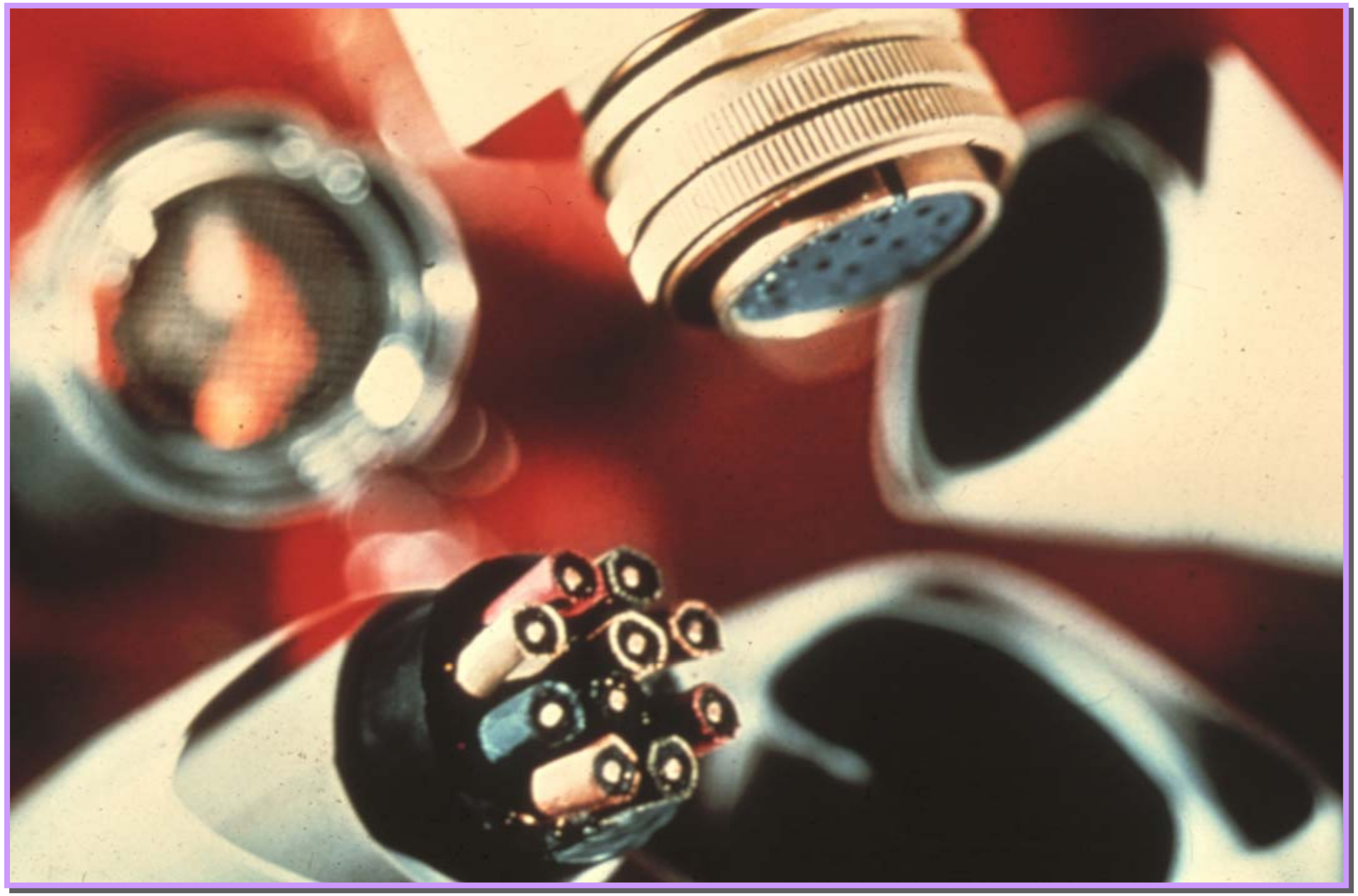


# Silicon Resin for Motor

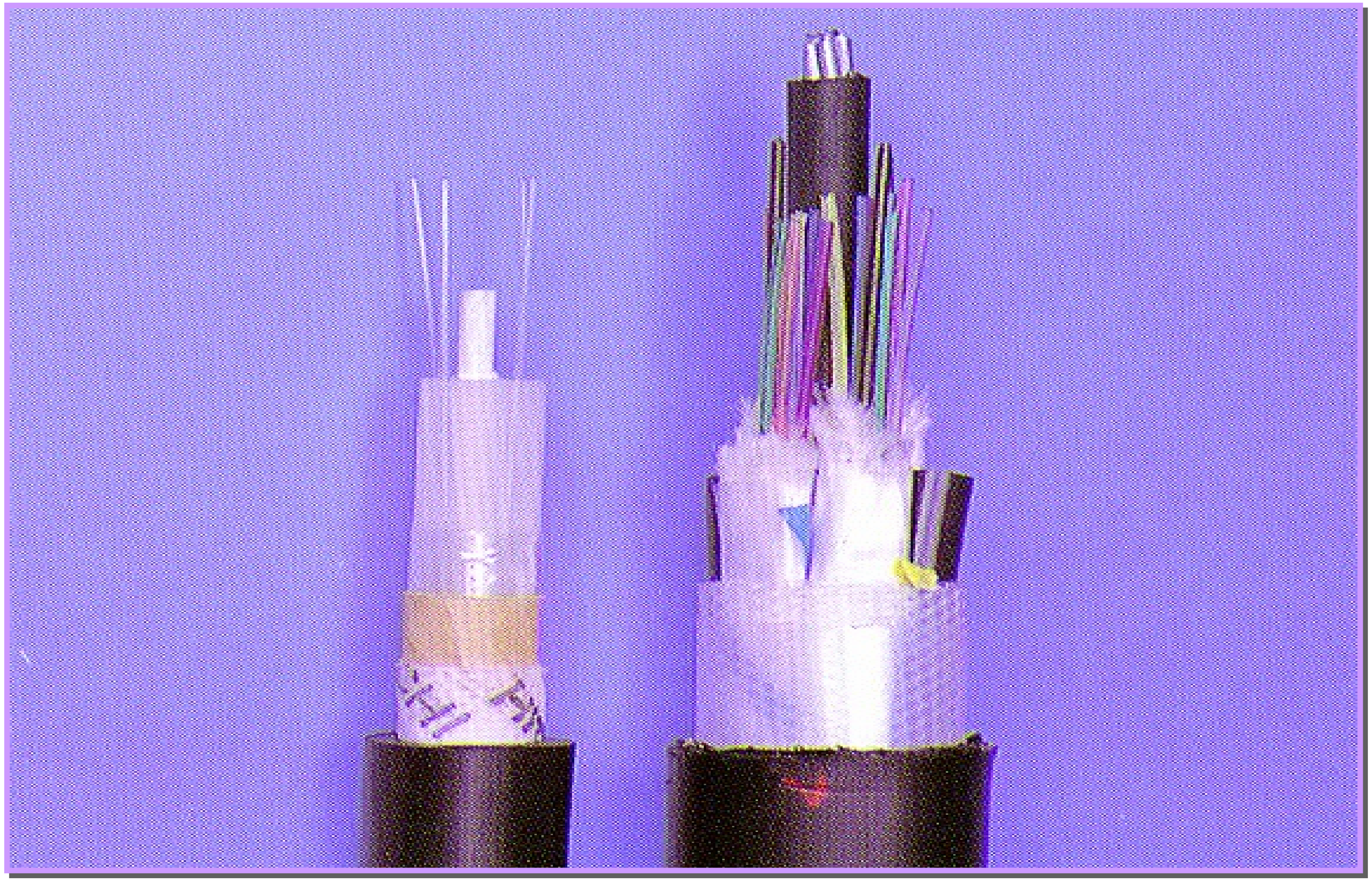
# Oil Seals



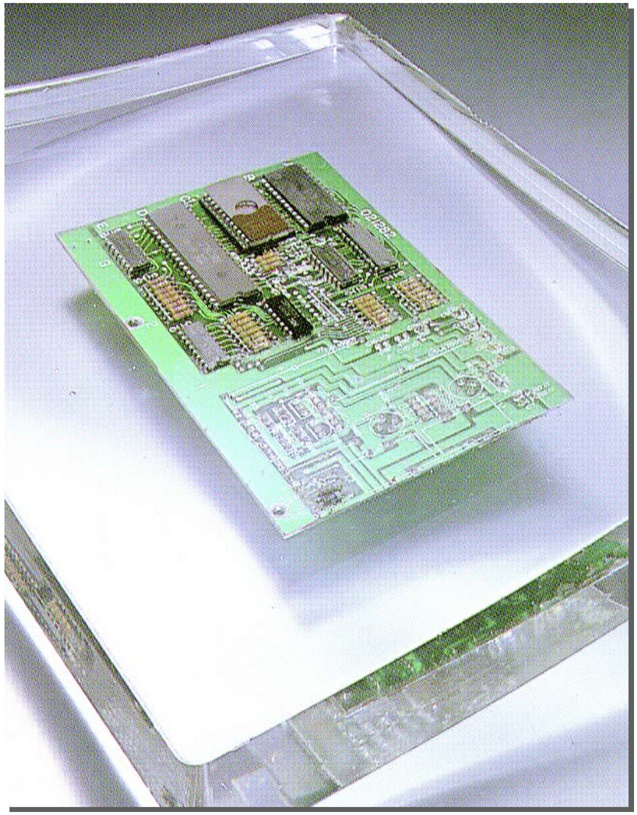
# Silicone Rubber Coated Cable

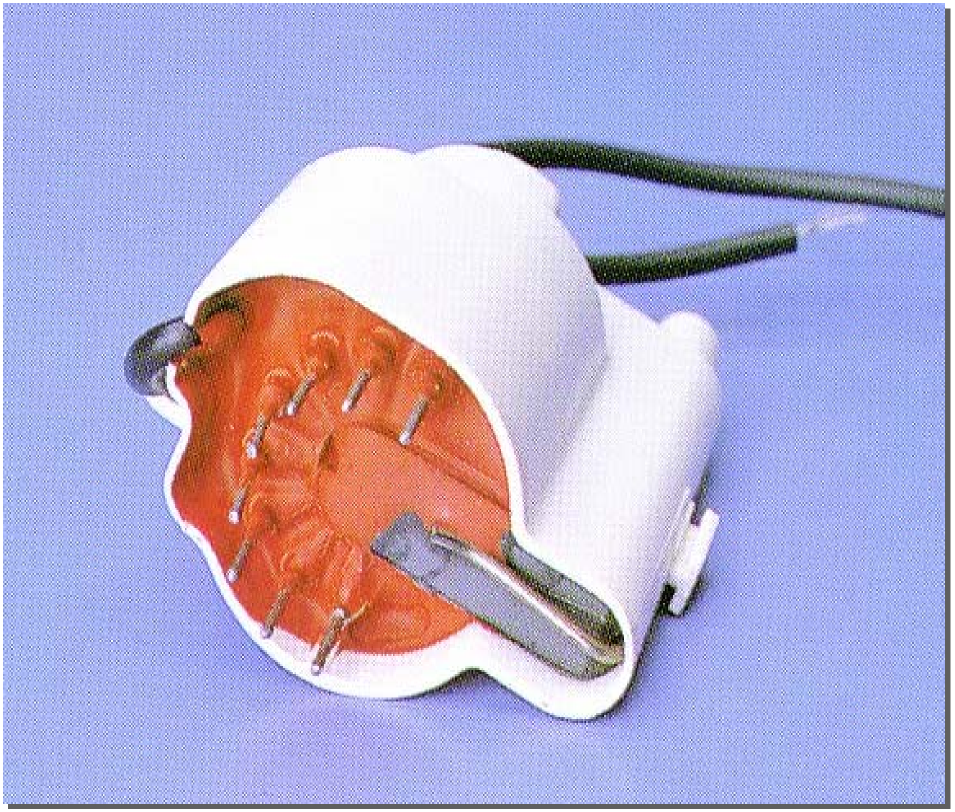


# Optical Fiber Cable



# Potting Electric and Electronic Appliances





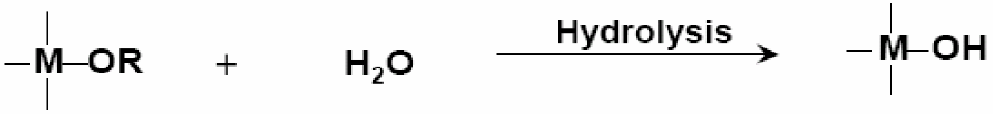
# Sol-Gel Chemistry

국립 공주대학교
Kongju National University

Prof. Jin-Heong Yim

# Sol-Gel Chemistry

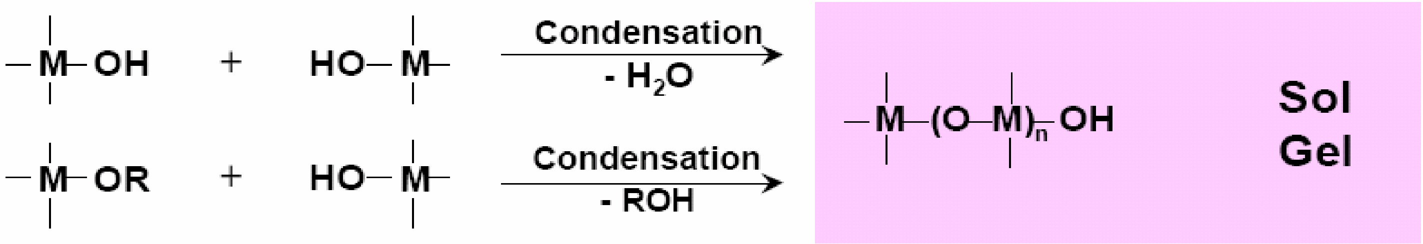
- **Hydrolysis**



$$-\mathrm{M}-\mathrm{OR} \quad + \quad H_2O \xrightarrow{\text{Hydrolysis}} -\mathrm{M}-\mathrm{OH}$$

M = Si, Al, Mg, Zr, Ti, In, Sn, etc.

- **Condensation**



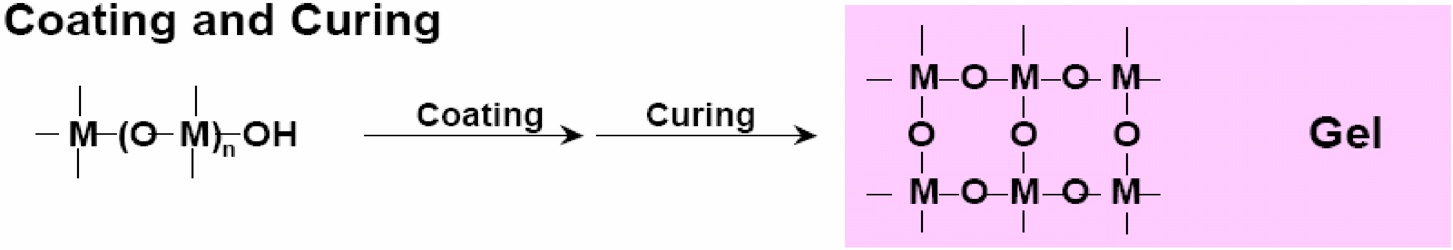
$$-\mathrm{M}-\mathrm{OH} \quad + \quad \mathrm{HO}-\mathrm{M}- \xrightarrow[\text{- }H_2O]{\text{Condensation}}$$

$$-\mathrm{M}-\mathrm{OR} \quad + \quad \mathrm{HO}-\mathrm{M}- \xrightarrow[\text{- ROH}]{\text{Condensation}}$$

$$-\mathrm{M}-(\mathrm{O}-\mathrm{M})_n-\mathrm{OH}$$

Sol
Gel

- **Coating and Curing**

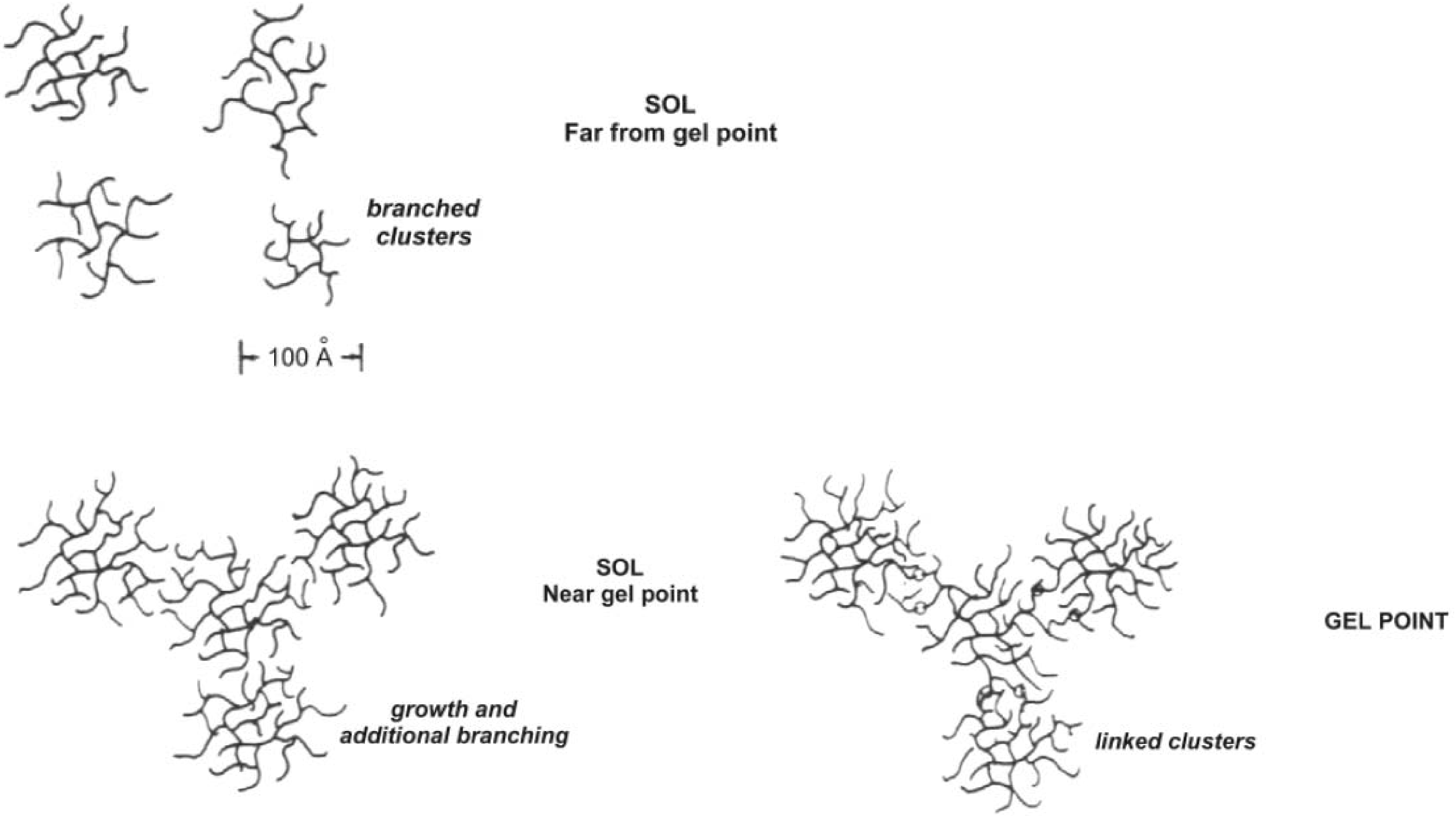


$$-\mathrm{M}-(\mathrm{O}-\mathrm{M})_n-\mathrm{OH} \xrightarrow{\text{Coating}} \xrightarrow{\text{Curing}}$$

$$\begin{array}{ccccccc} - & \mathrm{M} & - \mathrm{O} - & \mathrm{M} & - \mathrm{O} - & \mathrm{M} & - \\ & | & & | & & | & \\ & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & \\ & | & & | & & | & \\ - & \mathrm{M} & - \mathrm{O} - & \mathrm{M} & - \mathrm{O} - & \mathrm{M} & - \end{array}$$

Gel

# Sol? Gel?


SOL
Far from gel point
branched clusters
100 Å
SOL
Near gel point
growth and additional branching
GEL POINT
linked clusters

# Sol? Gel?

- a **sol** where the polymerized structures do not reach macroscopic sizes
- a **gel** when the recombination of the metal oxo polymers can produce bushy structures which invade the whole volume inside which the solvent, reaction by-products and free polymers are trapped
- a **precipitate** when the reactions produce dense rather than bushy structures

Depending on the control of the structures of these oxo polymers through

# General Mechanism

Based on the growth of **metal oxo polymers** in a solvent

- inorganic step polymerization reactions through hydrolysis and condensation of metal alkoxides $M(OR)_Z$, where M = Si, Ti, Zr, Al, Sn, Ce…, OR is an alkoxy group and Z is the valence or the oxidation state of the metal
- first step : hydroxylation upon the **hydrolysis** of alkoxy groups :

$$M\text{-}OR + H_2O \rightarrow M\text{-}OH + ROH$$

- second step : polycondensation process leading to the formation of branched oligomers and polymers with a metal oxo based skeleton and reactive residual hydroxo and alkoxy groups ; 2 competitive mechanisms :

# General Mechanism

- **oxolation** : formation of oxygen bridges :

$$M\text{-}OH \quad + \quad XO\text{-}M \quad \rightarrow \quad M\text{-}O\text{-}M \quad + \quad XOH$$

where X = H, generally when **hydrolysis ratio h** = $H_2O/M >> 2$
or X = R, when h = $H_2O/M < 2$

- **olation** : formation of hydroxo bridges when the coordination of the metallic center is not fully satisfied ($N - Z > 0$) :

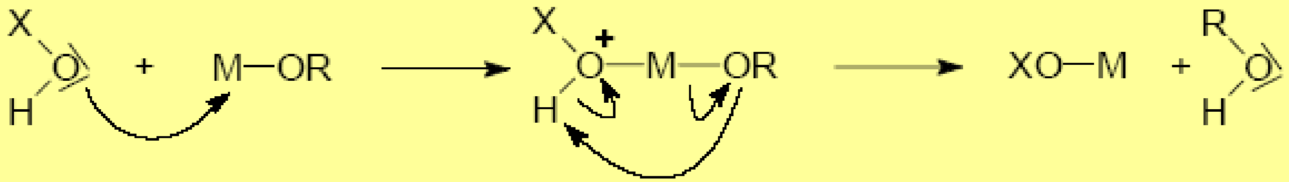
$$M\text{-}OH \quad + \quad HO\text{-}M \quad \rightarrow \quad M\text{-}(OH)_2\text{-}M \qquad \text{where } X = H \text{ or } R$$

The kinetics of olation are usually faster than those of oxolation

# Chemical Reactivity

$$M(OR)_n \; + \; m\,XOH \rightarrow [M(OR)_{n-m}(OX)_m] \; + \; m\,ROH$$

where X stands for H (hydrolysis), M (condensation) or L (complexation by an organic ligand L)



| | | | |
|---|---|---|---|
| oxidation state : | **Z** | **Z-1** | **Z** |
| coordination number : | **N** | **N+1** | **N** |

Consequently, the chemical reactivity of metal alkoxides toward nucleophilic reactions mainly depends on :

- the strength of the nucleophile
- the electrophilic character of the metal atom (an electronegativity-related property characterized by the positive charge on the metal atom)

# Chemical Reactivity

- its ability to increase its coordination number N : the degree of unsaturation of the metal coordination can be simply expressed by the difference N - Z, where N is the coordination number usually found in the oxide and Z is the oxidation state

| alkoxides | $\chi$ | partial charge $\delta$ | ionic radius (Ă) | oxide | N | N - Z |
|---|---|---|---|---|---|---|
| $Si(OPr^i)_4$ | 1.74 | + 0.32 | 0.40 | $SiO_2$ | 4 | 0 |
| $Sn(OPr^i)_4$ | 1.89 |  | 0.60 | $SnO_2$ | 6 | 2 |
| $Ti(OPr^i)_4$ | 1.32 | + 0.60 | 0.64 | $TiO_2$ | 6 | 2 |
| $Zr(OPr^i)_4$ | 1.29 | + 0.64 | 0.87 | $ZrO_2$ | 7 | 3 |
| $Ce(OPr^i)_4$ | 1.17 | + 0.75 | 1.02 | $CeO_2$ | 8 | 4 |

For similar alkoxy groups OR :

$$Si(OR)_4 \lll Sn(OR)_4$$

$$\text{and} \quad Ti(OR)_4 < Zr(OR)_4 < Ce(OR)_4$$

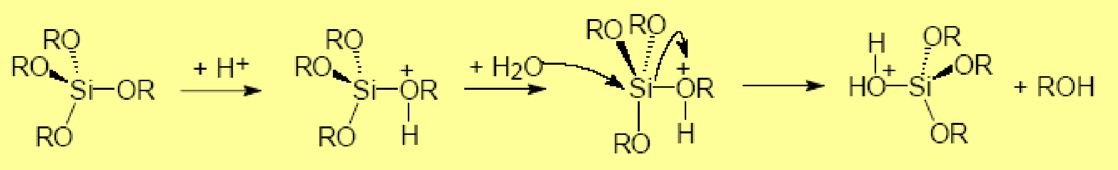
# Chemical Reactivity

- **silicon** : relatively low electrophilicity and N - Z = 0 ; thus, silicon alkoxides are not very reactive : hydrolysis-condensation reaction rates must be increased by catalysts
- **tin** : higher electrophilic power and higher degree of unsaturation N – Z
- **titanium, zirconium and cerium** : lower electronegativity, but very high degree of unsaturation N – Z

Hydrolysis and condensation reactions of non-silicate metal alkoxides must be controlled by using chemical additives

# Reactivity of Si

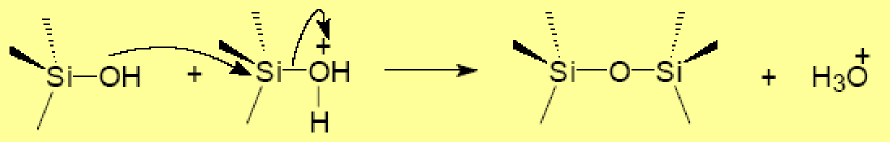
**Under acidic conditions** (e.g. with mineral acids), the hydrolysis reaction is speeded up more efficiently than the condensation reaction :



*protonation of the alkoxo group, making alcohol a better leaving group*

Condensation involves the attack of silicon atoms carrying protonated silanol species by neutral ≡Si-OH nucleophiles

- acidic conditions further the formation of protonated silanol species, but inhibit some nucleophiles
- the most basic silanol species (the most likely to be protonated) are those contained in monomers or weakly branched oligomers :



*preferentially a monomer*
*or the end-group of a macromolecule*

So a bushy network of weakly branched polymers is obtained

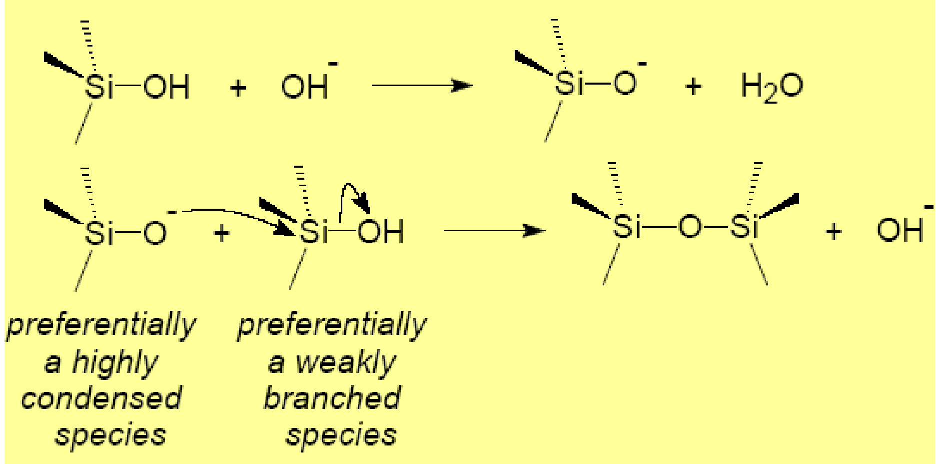
# Reactivity of Si

**Under basic conditions** (e.g. with ammonia), hydroxyl anions ($OH^-$) and deprotonated silanol (≡Si-$O^-$) are better nucleophiles than water and silanol species

- ➢ a fast attack at the silicon atom and both hydrolysis and condensation reactions occur simultaneously

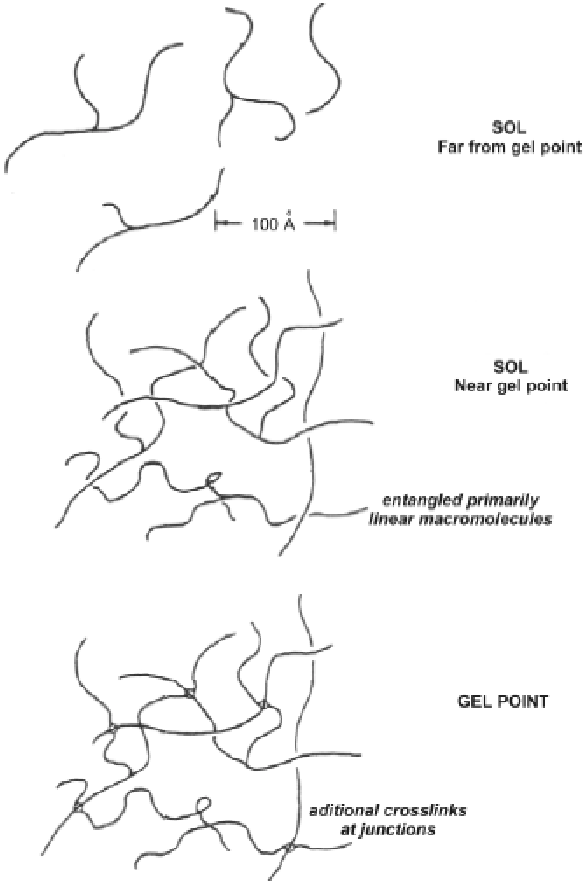
The condensation involves the attack of a deprotonated silanol (≡Si-$O^-$) on a neutral siloxane species

- ➢ the acidity of silanol increases when -OH or -OR groups are replaced with -O-Si≡ groups because of the reduced electron density on Si atom

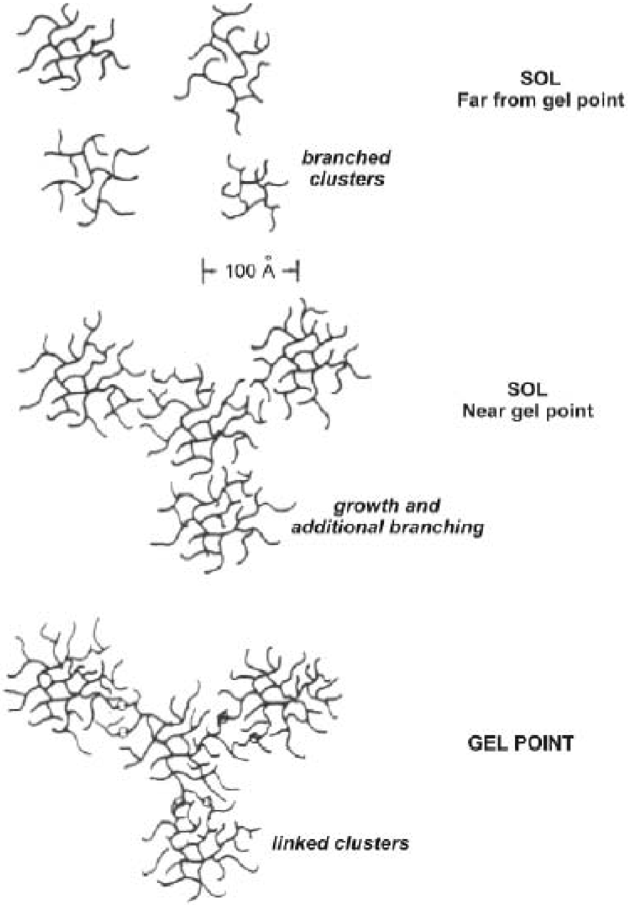


# Gelation

## Acid Catalyzed Polymerization



## Base Catalyzed Polymerization



# Aging

**Aging** : structure modifications with time depending on temperature, solvent and pH conditions

- gel separation into regions of high and low polymer density because it is expected that as the critical point is approached (e.g. during a change in concentration), fluctuations in polymer density grow larger in amplitude (than those resulting merely from thermal motions)
- promotion of additional crosslinking as unreacted terminal groups (OH and OR) come in contact in regions of higher polymer density
- acceleration of the **phase separation** process and creation of **liquid-solid interfaces**
- further structural changes attributed primarily to surface energy effects : it is well known that surfaces exhibiting positive radii of curvature dissolve more readily than surfaces exhibiting negative radii of curvature. Therefore as the dissolution rate is increased (e.g. by increased temperature or pH) dissolution-redeposition results in **neck formation** causing the gel structure to become **fibrillar** and the **pore formation**. Of course, when dissolution is extensive, the gel network would break down and ripen to form a colloidal sol.

# Drying

## c) drying (or desiccation)

**Drying** : removing of the solvent phase

Method influenced by the intended use of the dried material :

■ if **powdered ceramics** are desired, no special care need be exercised to prevent fragmentation

■ if **monoliths from colloidal gels** are desired, the drying procedures are largely determined by the need to minimize internal stresses associated with the volume changes on drying and the capillary forces in the gel pores :

- during the initial stages of drying, the volume change of the gel is equal to the volume of evaporated liquid. The gel network is still flexible and can rearrange to accommodate the decreasing volume. All pores are filled with solvent and liquid-air interfaces are not present
- as drying proceeds, the gel network becomes more restricted and the removal of liquid leads to the formation of such interfaces and the development of capillary stresses : the capillary pressure $\Delta P$ developed in a cylindrical capillary of radius r partially filled with a liquid of wetting angle $\theta$, can be expressed by :

  $$\Delta P = 2\gamma\cos\theta/r$$

  where $\gamma$ is the surface tension. The development of cracks in a drying gel is shown on figure 5 :

# Stress Formation

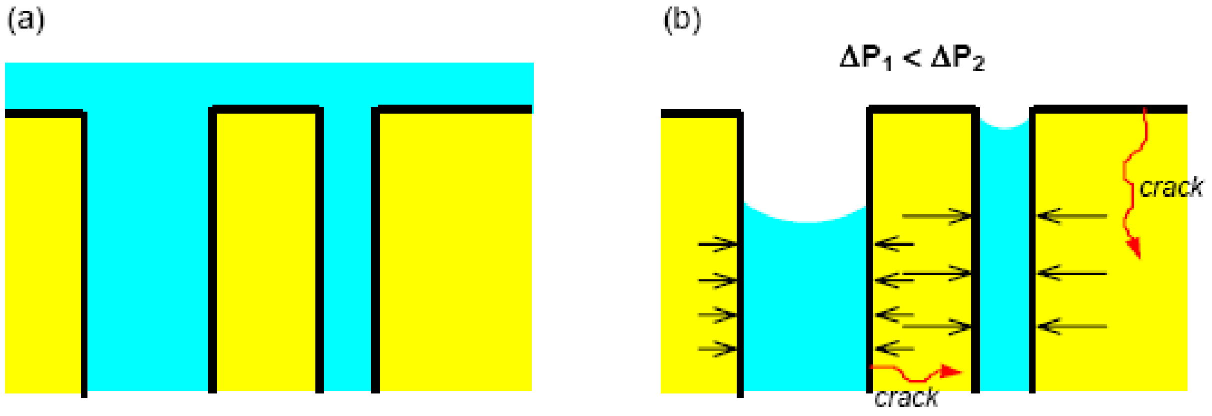


**Figure 5 :** Formation of differential strains at the pores during drying : (a) before and (b) after the onset of capillary forces.

# Drying

- operating under **hypercritical conditions** : effected by heating the gel with methanol in an autoclave to temperatures and pressures exceeding the critical point of methanol (240°C/8.1MPa). A slow evacuation (3-4 hr) was followed by flushings with dry argon to eliminate the last traces of alcohol. This method produces dried gels with much larger pore volumes (**aerogels** : porosity of ~85 %, specific surface area of 250-600 $m^2.g^{-1}$ and pore size of 250-1250 Å) than conventional evaporative drying (**xerogels** : pore size $\leq$ 20 Å). Because of the absence of the liquid-vapor interfaces, no capillary forces arise to cause network collapse and shrinkage during drying

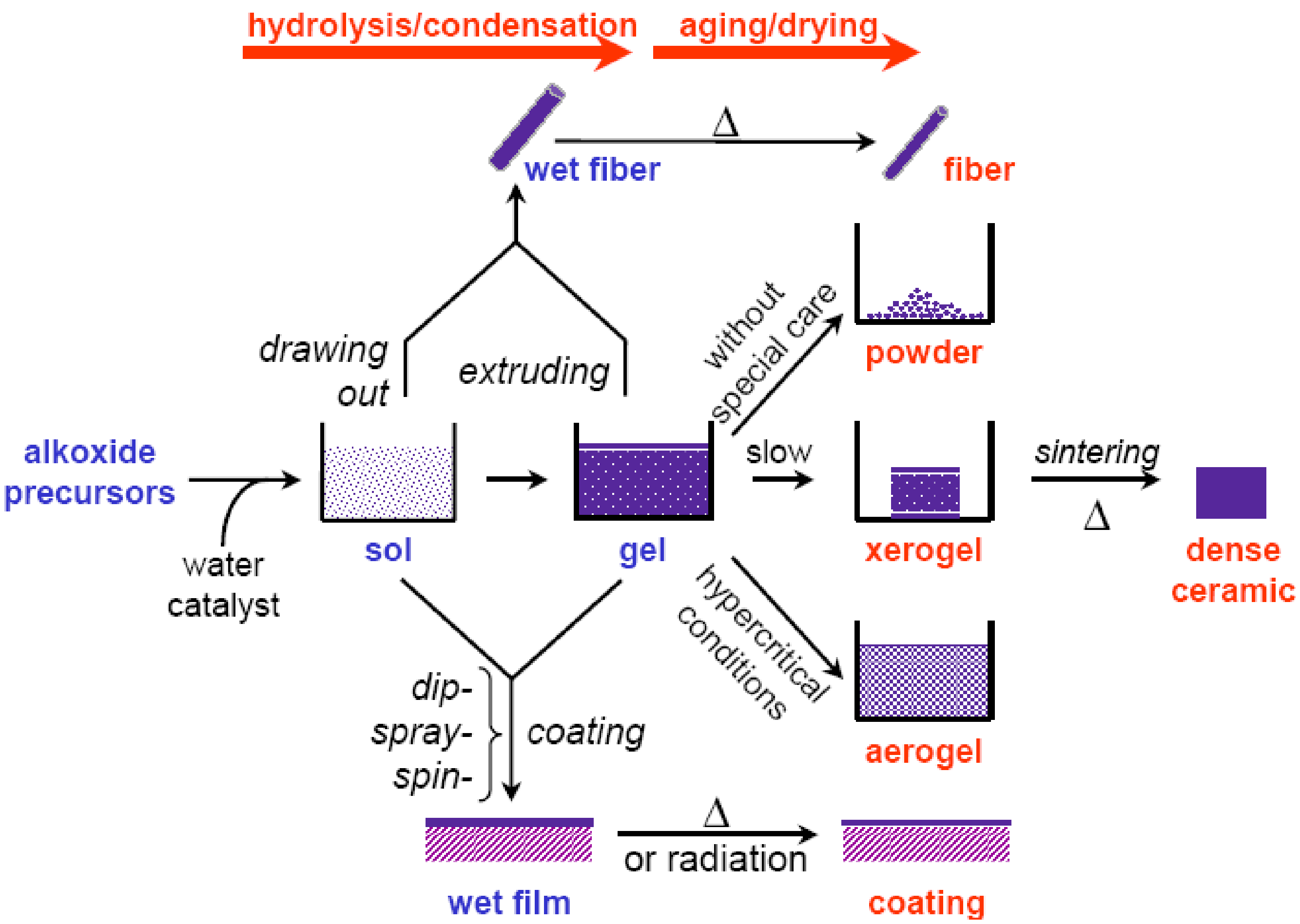
# Firing

**Firing** : heating to convert the dried gel to a dense ceramic. For silica gels, the following reactions occur :

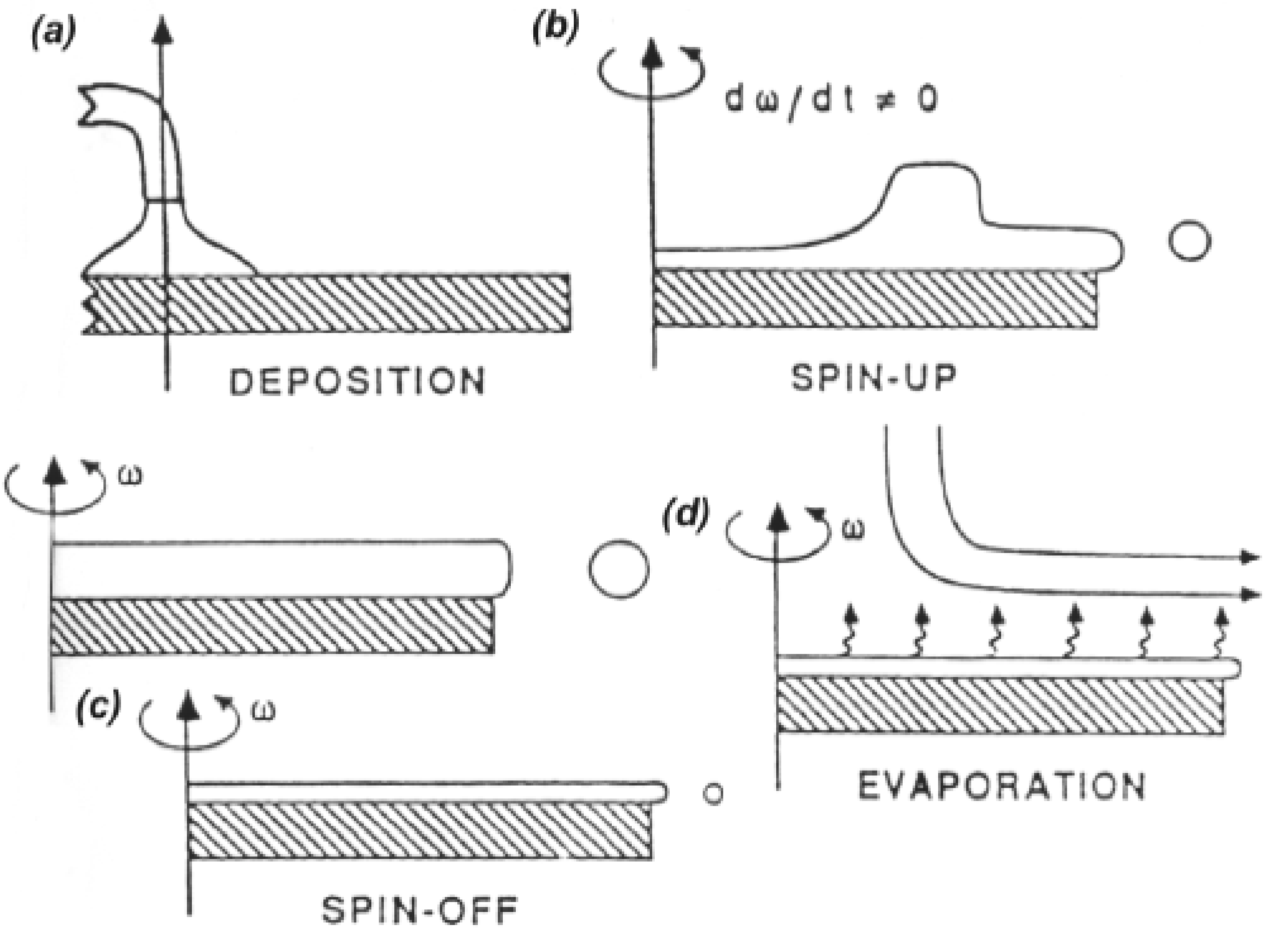
- desorption of physically adsorbed solvent and water from the walls of micropores (100-200°C)
- decomposition of residual organic groups into $CO_2$ (300-500°C)
- collapse of small pores (400-500°C)
- collapse of larger pores (700-900°C)
- continued polycondensation (100-700°C)

# Summary

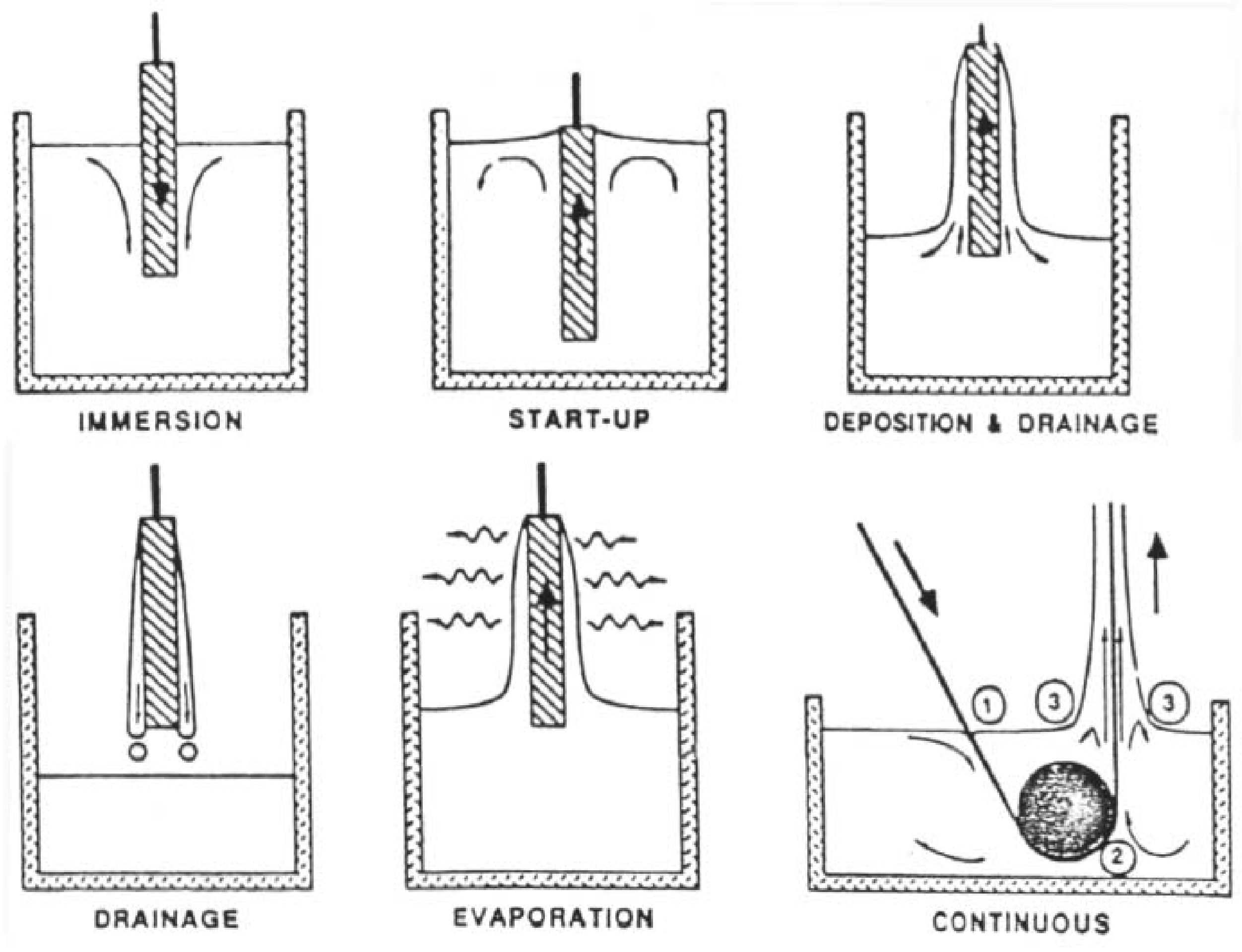
summary of sol-gel process, techniques and products



# Spin Coating



# Dip Coating


IMMERSION
START-UP
DEPOSITION & DRAINAGE
DRAINAGE
EVAPORATION
①
③
③
②
CONTINUOUS

# Dip Coating Process

Figure 6 : Industrial dip-coating system

# Coating Applications

- antireflection coatings (single layer or multilayer films)
- absorbing coatings
- filters for lighting and optical purposes
- semiconducting coatings
- protective layers (both chemical and thermal)